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An Infrared Study of CO Adsorption on Magnesia-Supported Ruthenium, Gold, and Bimetallic Ruthenium–Gold Clusters

J. SCHWANK,[1] G. PARRAVANO,[2] AND H. L. GRUBER[3]

Institut für Physikalische Chemie der Universität Innsbruck, A-6020 Innsbruck, Austria

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The adsorption of carbon monoxide on magnesia-supported ruthenium, gold, and bimetallic ruthenium/gold samples of varying composition was studied by infrared spectroscopy. The effects of different sample pretreatments, varying CO coverages, and coadsorption of hydrogen and oxygen on band frequencies and relative and integrated band intensities are reported. On the basis of these results and in comparison with results obtained for ruthenium on silica, consistent assignments have been made for all the bands observed in the spectra. Evidence for support–metal interaction in the pure metal samples, for metal–metal interaction in the bimetallic sample, and thus for the existence of bimetallic Ru–Au clusters is presented.

INTRODUCTION

Highly dispersed supported gold preparations revealed considerable catalytic activity in recent investigations of hydrogen and oxygen transfer reactions (*1–4*). The results of extended X-ray absorption fine structure spectroscopy (EXAFS) studies (*5*) and the significant differences in the selectivity and activity of gold catalysts supported on SiO_2, Al_2O_3, or MgO, respectively (*4*), indicated the presence of strong metal–support interactions influencing the oxidation state of the highly dispersed gold. With regard to these findings and in order to elucidate further the role of electronic interactions between gold and support materials it seemed to be of interest to extend the investigation to supported bimetallic systems, such as Au–Pt (*6*) and Au–Ru (this study).

In any work on alloys or bimetallic clusters, the question of surface composition, possible metal segregation, and component interaction is of utmost importance. Detailed reviews of the general principles and problems involved have been given by Sachtler (*7*), Sinfelt (*8*), and Ponec (*9*). One means of characterization of the surface properties of bimetallic clusters is a study of the infrared spectra of adsorbed carbon monoxide as it was first applied to the Cu/Ni system by Eischens (*10*), to the Pd/Ag and the Cu/Ni system by Soma-Noto and Sachtler (*11, 12*), and to the Ru/Pt system by Brown and Gonzalez (*13*). The assignment of the infrared bands resulting from the adsorption of carbon monoxide on a bimetallic system requires detailed knowledge of the behavior of carbon monoxide adsorbed on the single metal components.

The peculiar role of ruthenium surfaces in the preferential formation of C–C bonds from mixtures of carbon monoxide and hydrogen has been known for several decades. The behavior stands in contrast to that of all other metals and metallic compounds tested. In spite of the inherent practical interest in the production of long chain hydrocarbons and oxygenated derivatives there is, as yet, no clarification of the effect in terms of known surface chemical and physical phenomena. Previous infrared studies of CO adsorbed on alumina or silica-supported ruthenium catalysts contain conflicting data and band assignments (*14–21*). Concerning gold there have been only a few

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[1] Present address: Department of Chemical Engineering, The University of Michigan, Ann Arbor, Michigan 48109.

[2] Deceased on April 1, 1978.

[3] To whom correspondence should be addressed.

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infrared investigations of CO adsorbed on alumina or silica-supported gold preparations (*22–24*) and on gold films (*25–27*). Therefore, and in view of the different support used in this study, an infrared investigation of CO adsorbed on magnesia-supported ruthenium and gold was a prerequisite for the ir characterization of bimetallic magnesia-supported ruthenium–gold preparations.

EXPERIMENTAL

The catalyst samples were prepared[4] by impregnation or coimpregnation of MgO (reagent grade, 15 m^2/g BET area) with $RuCl_3 \cdot H_2O$ or (and) $HAuCl_4 \cdot 3H_2O$, respectively, to give a total metal content of 5 wt%. After drying for 16 hr at room temperature and 4 hr at 115°C, reduction was carried out in flowing hydrogen for 2 hr at 300°C followed by 2 hr at 400°C. The composition as determined by atomic absorption is given in Table 1. Particle size distributions were determined by transmission electron microscopy. All samples investigated showed a fairly wide particle size distribution in the range of 30 to 60 Å. For a better comparison with published literature data, a sample of 5% Ru on SiO_2 was prepared, using Aerosil 130 as a support material. For the ir measurements the reduced catalysts were pressed to 20-mm disks of about 30 mg/cm^2. The disks were mounted in an all Pyrex ir cell on a movable support, so that they could be raised into the vertical part of the cell, which was surrounded by an oven and could be heated to 500°C. Sodium chloride windows were sealed to the cell using heat-shrinkable tubing (*28*). All spectra were recorded with the sample at room temperature on a Perkin Elmer 180 filter grating spectrophotometer. Infrared absorption by the support material was partially compensated for by using an identical sample disk in a second Pyrex cell in the reference beam. The gases used were purified in cold traps, except for carbon monoxide, where a research grade CO of 99.997 vol% (Messer-Griesheim) was used as received.

TABLE 1

Catalyst Composition

Sample	Support	Metal content (wt%)	Gold content (at%)
Ruthenium	SiO_2	5.0	0
Ruthenium	MgO	2.1	0
Ruthenium	MgO	4.4	0
Ru/Au	MgO	4.3	11
Ru/Au	MgO	4.5	36
Ru/Au	MgO	4.7	90
Gold	MgO	3.5	100

After mounting in the ir cell, all samples were first purged in flowing helium, raising the temperature to 100°C. Then helium was replaced by hydrogen, the temperature raised to 300°C over a period of 2 hr and held there for another 2 hr. The further pretreatment followed three different procedures: Cooling to room temperature (1) in flowing H_2; (2) in flowing He; (3) in flowing He, followed by a short exposure to 35 Torr of oxygen. Samples pretreated according to the first procedure will be referred to as "hydrogen-covered," those from the second pretreatment as "bare," and those of the third procedure as "oxidized." After the chosen pretreatment the samples were evacuated and then exposed to 35 Torr of CO for 15 min at room temperature. Spectra were then recorded (1) in presence of gas phase CO (35 Torr), (2) after reduction of the CO-pressure to 0.1 Torr, (3) after evacuation and 15 min He-purge at room temperature, (4) after thermal desorption in He (70/140/200/245°C), and (5) after coadsorption of H_2 or O_2 on the CO-covered surface.

RESULTS AND DISCUSSION

Ru/MgO

In view of the differences previously observed in the spectra of CO on ruthenium which were partly ascribed to different de-

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[4] Preparation of all samples used was carried out by Dr. G. Tauszik at Istituto G. Donegani in Novara, Italy and is gratefully acknowledged.

grees of reduction of the metal surface (*19*), a special effort was made to obtain spectra on fully reduced surfaces as well as on surfaces deliberately exposed to oxygen, as represented by the pretreatments (1) and (3) described above. Typical spectra obtained on these two types of ruthenium surfaces are shown in Figs. 1 and 2. With the "hydrogen-covered" surface—which under our conditions should represent a fully reduced surface—only one strong asymmetric band is observed in the presence of 0.1 Torr CO, with a maximum at 2035 cm^{-1} shifting to 2020 cm^{-1} upon evacuation. On the "oxidized" surface two additional bands are found at 2080 and 2130 cm^{-1}. In contrast to the low-frequency band at 2020 cm^{-1}, these two bands show practically no frequency dependence on coverage. The same dependence or lack of dependence of frequencies on coverage is found when the coverage is decreased by thermal desorption. In addition, the total integrated band intensity on the oxidized surface is substantially lower then the one on the reduced surface.

The spectra obtained on the "bare" surface (see, for example, spectrum b of Fig. 4) are similar to those observed on the oxidized surface, showing all three bands at 2030, 2080, and 2130 cm^{-1}. In contrast to the "oxidized" surface, where the band at 2080 cm^{-1} is the most intensive one, it is now the low-frequency band at 2030 cm^{-1}, which is much more intense than the other two. The spectra shown in Figs. 1 and 2 imply already that the low-frequency band should be ascribed to CO on a reduced surface, the other two bands to CO on an "oxidized" surface, as has been suggested before by Brown and Gonzalez (*19*). However, under reduction conditions comparable to the ones used here, all three bands were consistently observed in recent work on highly dispersed ruthenium. Thus, the occurrence of one band only on our hydrogen-covered surface might be connected with the fact that a different support, namely MgO, was used in the present study. Therefore, we also took some spectra with ruthenium on silica. There, even on the hydrogen-covered surface, all three bands could indeed be observed. The most straightforward interpretation of this difference is simply to assume that the re-

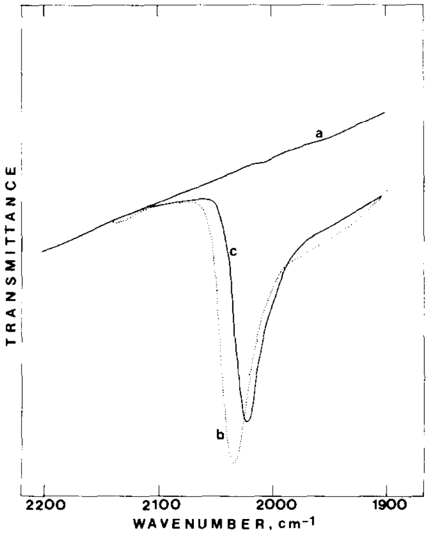

FIG. 1. Infrared spectra of CO adsorbed on 4.4% Ru/MgO at 25°C after pretreatment 1 ("hydrogen-covered"): (a) background, (b) after exposure to CO and evacuation to 0.1 Torr, (c) after 15 min evacuation.

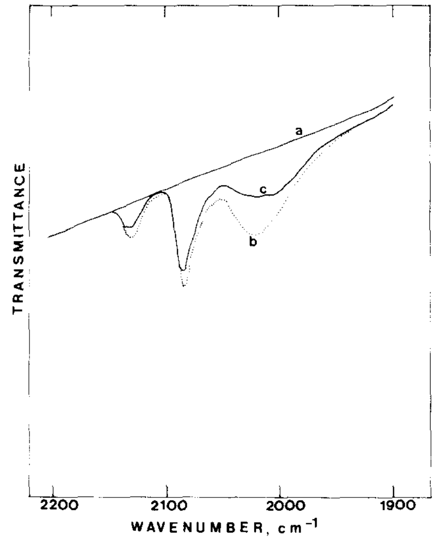

FIG. 2. Infrared spectra of CO adsorbed on 4.4% Ru/MgO at 25°C after pretreatment 3 ("oxidized"): (a) background, (b) after exposure to CO and evacuation to 0.1 Torr, (c) after 15 min evacuation.

duction of dispersed ruthenium is greatly facilitated by the MgO support, so that experimental conditions which lead to incomplete reduction for Ru/SiO_2 suffice for complete reduction of Ru/MgO. For ruthenium on alumina, Dalla Betta (*18*) obtained all three bands for samples with high metal dispersion, but only the low-frequency band for a sample of relatively low metal dispersion (particle size of about 90 Å). He interpreted the difference in terms of a particle size effect, assigning the low-frequency band to CO adsorbed on metal sites of high coordination (planes) and the other two bands to CO on sites of lower coordination, such as corner and edge atoms, whose contribution would of course diminish with increasing metal particle size. Brown and Gonzales already pointed out (*19*) that the three bands observed by Dalla Betta on Ru/Al_2O_3 might indicate a lack of complete reduction. In view of our results with SiO_2 and MgO supports we also think that the difference observed between different states of dispersion may be explained by a different degree of reduction. It is well known (*29, 30*) that, under given reducing conditions, the more highly dispersed metal is more difficult to reduce than samples of a lower degree of dispersion.

The gradual and completely reversible change in the spectra observed in this work with three different pretreatments of one sample of given particle size would be difficult to explain by surface rearrangements giving the necessary distribution of plane, edge, and corner sites to account for the relative intensities in which the three bands occur. In addition, the nature of the pretreatment also effects the total integrated intensity of the CO stretching bands. Procedure 2 yields only 70%, procedure 3 only about 50% of the intensity obtained after pretreatment 1. Even though a quantitative interpretation of integrated intensities is problematic and therefore not attempted throughout this paper, the above trend is considered as an indication of qualitative changes in coverage, an assumption which is fully supported by the observed frequency changes. Going from more reducing to more oxidizing pretreatment conditions, the band position of the low-frequency band shifts to lower wave numbers as shown in Fig. 3. Considering this frequency shift and the fact that a decrease of coverage by evacuation or thermal desorption also resulted in corresponding shifts to lower wave numbers, the changes in intensity with different pretreatment can safely be interpreted as being due to decreasing coverages. An interpretation of the intensity decrease in terms of a change of extinction coefficient would require a frequency shift in the opposite direction (*31*). Thus, the "bare" surface, and even more so the "oxidized" surface, show lower coverages with CO than the "H-covered" surface and it must be concluded that after pretreatment 2 and 3 the surface is partially blocked by oxygen and even on the MgO support a fully reduced ruthenium surface can only be maintained under hydrogen.

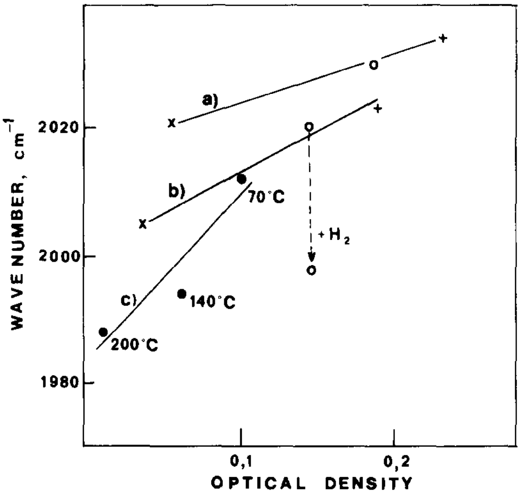

FIG. 3. Correlation between the position of the band maximum and the optical density log (I_0/I) of the low-frequency band of CO adsorbed on 4.4% Ru/MgO at 25°C after the three different pretreatments: (+) "hydrogen-covered," (O) and (●) "bare," (x) "oxidized" surface; (a) after exposure to CO and evacuation to 0.1 Torr, (b) after 15 min evacuation, (c) after thermal desorption at 70, 140, and 200°C (filled circles); the arrow indicates the effect of hydrogen coadsorption.

In order to gain additional evidence for the interpretation of the spectral features observed with different pretreatments, a series of experiments was carried out, coadsorbing hydrogen or oxygen onto the CO-covered surface and looking for corresponding changes in the spectra. Coadsorption of hydrogen onto a CO-covered surface, which had shown the typical spectrum after pretreatment 2 (see Fig. 4, spectrum b) results in a shift of the low-frequency band to lower wave numbers (see spectrum c in Fig. 4 and arrow in Fig. 3), while the positions of the other two bands remain unaffected. These two bands, however, show a distinct decrease in intensities, which might be due to a conversion of CO into the form responsible for the low-frequency band rather than due to desorption. A slight increase in intensity of the low frequency band is visible in the spectra (Fig. 4), however, a quantitative evaluation has not been attempted, since the expected increase would amount to only a few percent of the band intensity and would therefore be close to the experimental reproducibility.

Upon heating the sample in the presence of hydrogen, the medium and high-frequency bands disappear completely at 200°C (Fig. 4d), while the low-frequency band becomes even more intense. The final spectrum corresponds closely to the one obtained after CO adsorption on the "H-covered" surface, except for the distinct shift in band position to lower wave numbers, which occurs already upon the initial coadsorption of hydrogen. This shift to lower wave numbers at nearly constant or even increasing coverage cannot be due to the correlation between frequency and intensity shown in Fig. 3. It can be interpreted however in terms of a donor–acceptor interaction, a concept which has repeatedly been used to explain CO frequency shifts observed after coadsorption of other molecules (see, e.g., Ref. *32*).

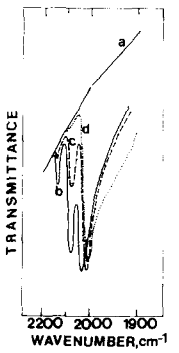

FIG. 4. Infrared spectra of CO adsorbed on 2.1% Ru/MgO at 25°C after pretreatment 2 ("bare" surface): (a) background, (b) after exposure to CO and 15 min evacuation, (c) after coadsorption of hydrogen at 25°C, (d) after heating in the presence of hydrogen to 200°C.

In all experiments concerning the coadsorption of hydrogen, the spectral region of C–H stretching frequencies (2800–3100 cm^{-1}) was monitored, but never found to show indications of any bands within the sensitivity of the experimental set up. Thus chemisorbed hydrocarbon species did not form under the experimental conditions used in the coadsorption experiments. Exposure of the sample to hydrocarbons, such as methyl cyclopentane and *n*-hexane at room temperature, also yielded no evidence for chemisorbed species, in contrast to analogous experiments on platinum, where under identical conditions chemisorbed hydrocarbon species could be readily seen (*33*).

Coadsorption of oxygen changes the spectra drastically into a form very similar to the one obtained upon adsorption of CO on the "oxidized" surface after pretreatment 3. This means, that the intensity of the low-frequency band is substantially reduced by coadsorption of oxygen. On the basis of donor–acceptor interaction a frequency shift to higher wave numbers is to be expected from coadsorbed oxygen. With the low-frequency band such a shift would be largely masked by a shift in the opposite direction, inherently caused by the decreasing coverage.

Taking into account all the experimental facts discussed above, there is no doubt that the low-frequency band corresponds to CO adsorbed on reduced ruthenium, while the other two bands correspond to CO adsorption states on not fully reduced surface sites or to states which occur only in the presence of oxygen. In full agreement with previous work we therefore assign the low-frequency band to carbon monoxide molecules adsorbed on zero-valent ruthenium. Whether this is a single, linear Ru–CO species as suggested by Brown and Gonzalez (*19*) or adsorption of several carbon monoxide molecules on one metal site, as proposed by Kobayashi (*17, 34*), cannot be definitely decided at present. However, in view of our evidence from relative intensities and considering the known ruthenium carbonyl spectra, we believe that the low-frequency band—at least as observed on a fully reduced surface after pretreatment 1—represents primarily a Ru(CO)$_x$ species, with x in the range of 2 to 4.

With such an assignment the observed frequency shift of the low-frequency band with coverage is entirely consistent with the interpretation of Blyholder (*35*), who proposed that increasing coverage would increase the competition among CO molecules for backbonding electrons, thus weaken the metal–carbon bond, correspondingly strengthen the C–O bond, and shift the band position to higher wave numbers. However, other interpretations of the frequency shift, such as surface heterogeneity and (or) dipol–dipol adsorbate interactions (*36–41*), cannot be excluded.

Concerning the specific assignments of the medium and high frequency bands, it has been suggested (*21*) that these two bands represent the symmetric and asymmetric stretching mode of two CO molecules adsorbed on a single oxidized ruthenium site. In the present work the relative intensities of these two bands depended strongly on the type of pretreatment (see "oxidized" and "bare" surface, Figs. 2 and 4) and were also significantly changed by oxygen coadsorption and by thermal desorption experiments. Thus, these two bands have to be assigned to two different surface species. On the basis of the observed changes of relative intensities with different surface pretreatment and with coadsorption of oxygen, it is suggested that the medium frequency band corresponds either to CO chemisorbed on zero-valent ruthenium, perturbed by chemisorbed oxygen or to CO chemisorbed on monovalent ruthenium, and that the high-frequency band represents CO adsorbed on Ru^{2+} or ruthenium oxide sites.

Au/MgO

The spectra obtained for CO adsorbed on MgO-supported gold after the three different types of pretreatment and after coadsorption of oxygen are shown in Fig. 5. While in previous work on dispersed gold (*24*) as well as on gold films (*25–27*) a band position between 2110 and 2115 cm^{-1} was found, the present work on MgO-supported gold gives a significantly lower frequency of 2085 cm^{-1} for the "H-covered" surface, 2100 cm^{-1} for the "oxidized" surface and 2105 cm^{-1} after oxygen coadsorption. Due to the weak adsorption of carbon monoxide on gold, which is entirely reversible at room temperature, the spectra of CO adsorbed on gold reported here had to be recorded at higher CO pressures in the order of 5 Torr. In spite of the higher pressure used, the coverage on gold was substantially lower than that on ruthenium. In agreement with previous work (*24–27*) the band position

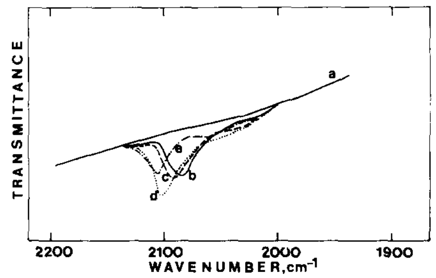

FIG. 5. Infrared spectra of CO adsorbed on 3.5% Au/MgO after exposure to CO and evacuation to 5 Torr at 25°C, showing the effect of different pretreatments and of oxygen coadsorption: (a) background, (b) "hydrogen-covered" surface, (c) "bare" surface, (d) "oxidized" surface, (e) after coadsorption of oxygen at 25°C.

was found to shift very slightly (5 to 10 wave numbers) to higher wave numbers with decreasing coverage. Therefore, differences in coverage cannot account for the differences in band position between CO adsorbed on silica-supported gold (*24*) or on bulk gold (*25–27*) on one side and CO adsorbed on magnesia-supported gold on the other side. Again, as in the case of ruthenium, one has to assume a specific carrier effect owing to the nature of the magnesium oxide support material. A similar effect of magnesium oxide was reported by Pritchard (*42*) for supported copper and was interpreted in terms of a preferred orientation of the metal crystallites. As with ruthenium, the effects of "reducing" and "oxidizing" pretreatments are completely reversible. The "oxidizing" pretreatment 3 and (or) the coadsorption of oxygen shifts the band position by 15 to 20 wave numbers to higher frequencies and thereby compensates the frequency shift to lower wave numbers, caused by the magnesium oxide support. After prolonged exposure to oxygen, the CO band was reduced in intensity and CO_2 appeared in the gas phase.

Ru/Au on MgO

The spectra of CO chemisorbed on the ruthenium rich sample (89 at% Ru, 11 at% Au) are generally very similar to those obtained on pure ruthenium. Pretreatment 2 and 3 yielded spectra which are practically indistinguishable from the corresponding spectra on pure ruthenium. With the "H-covered" surface of pretreatment 1 a strong single band with a maximum at 2030 cm^{-1} is found, without any evidence at all for a band corresponding to CO adsorbed on gold. With all gold-containing samples spectra were also taken at the higher CO pressure of about 5 Torr, since the results on pure gold had shown that upon evacuation to 0.1 Torr, CO desorbs from the gold surface to such a degree that bands are no longer visible. In contrast, the bands of CO adsorbed on ruthenium show only a minor decrease in intensity upon pumping, as can be seen in Figs. 1 and 2. This difference in the desorption behavior of CO on Ru and CO on Au affords an easy means of distinguishing between these two types of bands, in addition to the band position which of course might be affected by any ruthenium–gold interaction.

The spectra obtained on the sample containing 64 at% Ru and 36 at% Au still exhibit the same general features as those of pure ruthenium. Adsorption on the "bare" and "oxidized" surface gave the three bands typical for CO adsorbed on a not fully reduced ruthenium surface. Compared to pure ruthenium, however, differences are apparent in band position, relative band intensities, and in the occurrence of additional shoulders in the spectrum. The spectra on the "H-covered" surface (Fig. 6) also exhibit the three bands, in contrast to the low Au or pure Ru sample, where this pretreatment gave the low-frequeny band only. Thus, this bimetallic sample on the MgO support gives a spectrum very similar

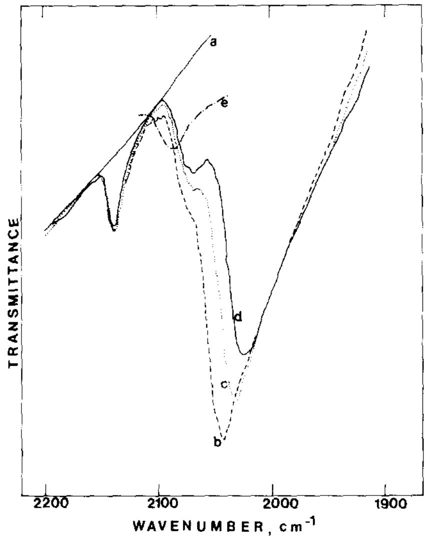

FIG. 6. Infrared spectra of CO adsorbed on a magnesia-supported bimetallic sample (4.5 wt% metal), containing 64 at% ruthenium and 36 at% gold at 25°C after pretreatment 1 ("hydrogen-covered"): (a) background, (b) after exposure to CO and evacuation to 5 Torr, (c) after evacuation to 0.1 Torr, (d) after 15 min evacuation, (e) for comparison: CO adsorbed on 3.5% Au/MgO after pretreatment 1.

to that of pure Ru on SiO_2. The occurrence of only the low-frequency band in the case of Ru on MgO was interpreted by the assumption that the magnesium oxide carrier facilitates the complete reduction of the metal. The occurrence of all three bands in the bimetallic sample would then indicate that this specific carrier effect is lost or compensated for by the addition of gold. Unquestionably, the presence of the high-frequency band at relatively high intensity means that with this bimetallic sample unreduced ruthenium is left even after pretreatment 1 on the "H-covered" surface. This finding certainly presents strong evidence for interaction between the two metal components.

As already observed for the low gold sample, even here, with a relatively high gold content of 36 at%, no evidence is found for a band which could be assigned to CO adsorbed on a gold site. Based on frequency alone, the band or shoulder at 2070 cm^{-1} (Fig. 6, spectrum b) might correspond to the CO band found on pure gold and shown for comparison in spectrum e of Fig. 6. However, the shoulder persists after evacuation to 0.1 Torr (Fig. 6, spectrum c) and shows up as a well-resolved band after further pumping (spectrum d). Therefore, it cannot be due to CO adsorbed on gold but clearly represents the medium frequency band of CO adsorbed on ruthenium. From the spectra shown in Fig. 6 it must then be concluded that, in this sample, gold is neither present in the form of segregated Au-clusters, nor does it cover the surface of the bimetallic clusters to an appreciable extent. Thus, the ruthenium–gold system seems to behave quite differently from the ruthenium–copper system, where, in accordance with theoretical expectations, a segregation of copper to the surface was postulated to explain catalytic activity and selectivity in a series of bimetallic samples (*43–45*). It should be kept in mind, however, that the samples investigated here were always exposed to CO for at least 15 min (time required to take the gas phase spectrum) before the first spectrum of adsorbed CO was recorded. Thus a segregation of ruthenium to the surface might occur under the influence of CO during this time (*46*).

The spectra of CO adsorbed on a gold-rich sample (90% Au) show a band at 2100 cm^{-1} which is easily removed by evacuation and therefore ascribed to CO adsorbed on gold. A further band around 2010 cm^{-1}, which is not removed on pumping, is assigned to CO adsorbed on zero-valent ruthenium, in correspondence with the 2030 cm^{-1} band on pure ruthenium. The difference in band position is to be expected on the basis of the low coverage and could be indicative of isolated ruthenium sites. Thus, it should not be taken as definite evidence for an "electronic" interaction between the two metals. However, the position of the CO–Au band at 2100 cm^{-1} for the "H-covered" surface and at 2110 cm^{-1} for the "oxidized" surface is consistently higher by 10 to 15 wave numbers than on pure gold at roughly equal coverages, a difference which indeed suggests an interaction between the two metal components.

CONCLUSIONS

(1) In contrast to CO adsorbed on Ru/SiO_2 or on Ru/Al_2O_3, CO adsorbed on Ru/MgO after reducing pretreatment at 300°C shows an infrared spectrum revealing only one strong band at 2030 cm^{-1}. This band is assigned to multiple CO adsorption on one single zero-valent ruthenium site. Two more bands at 2080 and 2130 cm^{-1} which appear in the spectrum of CO on silica-supported ruthenium under all conditions and on magnesia-supported ruthenium under less reductive pretreatment are assigned to two different CO species, both connected with oxygen, be it in the form of a perturbation by chemisorbed oxygen or in the form of chemisorption on monovalent or divalent ruthenium sites. On the basis of this assignment the observed shifts in frequencies and changes in relative and integrated band intensities as affected by (a) dif-

ferent pretreatment procedures, (b) coverage variations due to evacuation or thermal desorption, and (c) coadsorption of hydrogen and oxygen can be explained in a consistent manner.

(2) The ir spectrum of CO adsorbed on MgO-supported gold shows only one relatively weak band, which is easily removed by evacuation at 25°C. The band positions at 2085 and 2100 cm^{-1} for the "reduced" and "oxidized" gold surface, respectively, are distinctly lower than previously reported. The difference is ascribed to a specific effect of the MgO support, which was also apparent in the case of ruthenium.

(3) With the Ru/Au bimetallic samples only the high-gold sample showed the band typical for CO adsorbed on gold, while the other two samples exhibited only bands due to CO adsorbed on ruthenium. In all cases addition of the second metal component counteracts the effects of the MgO support, so that interaction of the two metals must be assumed. No evidence was found for separate Au clusters or for segregation of Au to the cluster surface. Results obtained with the sample of intermediate composition on the contrary indicate the existence of ruthenium adsorption sites only. Thus, just as previously found for ruthenium–copper catalysts (*44, 45, 47*), it must be concluded that true bimetallic Ru–Au clusters are present, although a large miscibility gap exists for this system in the bulk phase.

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